

THE ILMENITE LIQUIDUS AND DEPTHS OF SEGREGATION FOR HIGH-TI PICRITE GLASSES:
P.C. Hess, Department of Geological Sciences, Brown University, Providence, RI 02912

Lunar picrite glasses represent primitive and perhaps near primary liquids which have suffered only minor degrees of crystallization or near crustal modification (1). These glasses are multisaturated with olivine and orthopyroxene at pressures from 20-25 kb. I argue below that high TiO₂ mare glasses were indeed equilibrated with orthopyroxene and were segregated from the lunar mantle at mean depths of 400-500 km.

The glasses are typically modelled as products of relatively low degrees of melting of an hybridized source resulting from the overturn and mixing of the gravitationally unstable cumulate pile. But the models are neither unique nor, in some cases, correct.

Hughes et al (2), for example found that the trace element characteristics of Apollo 17 74220 orange glass could be obtained by melting 4-7% of an hybridized source formed of 95.8% early cumulate olivine and 4.2% late stage cumulates containing 24% augite, 40% plagioclase and 36% ilmenite plus much smaller amounts of apatite and highly evolved trapped KREEPy liquid. These results, however, are unacceptable if major elements are considered. A very powerful constraint is that ilmenite, augite, and plagioclase (or garnet) are not found near the high pressure liquidus of the orange glass 74220 (3). Thus melting must eliminate these phases from the source. The liquid produced by 4% melting and leaving only olivine in the residue must have about 20% TiO₂, and 13% Al₂O₃ and 11% CaO! Compare this liquid to the orange glass which has about 9% TiO₂, 6% Al₂O₃ and 7% CaO. The liquid produced by 7% melting is closer to the mark (11% TiO₂, 7% Al₂O₃, 6% CaO) but is not a good match for orange glass. It is clear from this example that the major and trace elements must be considered together in petrogenetic modelling. This abstract focuses on the constraints imposed by the TiO₂ content of high TiO₂ mare basalts.

Delano (4) determined the high pressure phase relations and the chemical composition of near liquidus minerals and melts of Apollo 15 red picrite glass. The results include the chemical compositions of ilmenite-saturated melts obtained from 1 bar to 20 kb. These compositions are now used to calculate the ilmenite saturation surface of Apollo 15 red glass over a wide range of pressures and temperatures

The solubility of ilmenite varies with pressure at fixed T°C as

$$(1) \ln x(T,P) = \ln x'(T,P') + \frac{\Delta \bar{V} \Delta P}{RT}$$

where $X(T,P)$ is the normative FeTiO₃ content of the melt at the T,P of interest, X' is the normative FeTiO₃ content of ilmenite saturated liquids (4) at T,P', $\Delta \bar{V}$ is equal to the difference in the molar volume of ilmenite and pure FeTiO₃ liquid and ΔP is equal to $P - P'$. Equation [1] ignores the variation in concentration of the MgTiO₃ component in ilmenite and assumes that the liquid activity coefficient, γ_{FeTiO_3} , is independent of pressure and FeTiO₃ content. The molar volume of ilmenite, the coefficient of thermal expansion and compressibility are from (5). The partial molar volumes, the partial molar coefficients of thermal expansion and compressibility of liquid TiO₂ and FeO are taken from (6,7). and are used to calculate the liquid molar volume of FeTiO₃.

Once the TiO₂ contents of ilmenite-saturated liquids are contoured with respect to pressure, the results are used to obtain the ilmenite saturated surface as a function of temperature at constant pressure. The TiO₂ contents of ilmenite-saturated picrite glasses are found for pressures up to 35 kb and temperatures from 1200-1500°C.

Table 1 gives the TiO₂ (wt%) contents of three picrite glasses under P-T conditions obtained at their liquidus. The liquidus of the Apollo 14 yellow glass was estimated using the empirical 1 bar liquidus (9) and a slope of 7% / kb. Table 2 gives the TiO₂ contents of melts along the ilmenite-lherzolite solidus (Mg* = 80). The solidus is estimated using $dT/d(Mg^*) = 9^\circ\text{C}/Mg^*$ and the constraint that the lherzolite solidus should occur at a higher temperature than that of mare basalt solidi. Note that the TiO₂ contents of ilmenite-saturated near solidus melts remain constant near 12% TiO₂ for $P = 15\text{-}30\text{ kb}$.

The three picrite glasses, TiO₂ contents from 4.6 to 13.5 wt%, (table 1) are strongly under-saturated with respect to ilmenite as confirmed by phase equilibria. Indeed, none of the picrite glasses (maximum TiO₂ = 16.4%) listed in (1) are in equilibrium with ilmenite under lunar conditions. Of even more significance, as discussed below, is that the TiO₂ contents of ilmenite saturated liquids at the lherzolite solidus, are greater than all but the most TiO₂-rich picrite glasses.

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Consider the melting of an Apollo 15 Red glass source. The near- solidus melt of ilmenite-lherzolite contains about 12% TiO₂. Melting must continue to temperatures to at least 30°C above the solidus to reproduce the TiO₂ contents of the red glass. But to produce a melt which is undersaturated with respect to ilmenite even higher super-solidus temperatures are required. For example, ilmenite saturated melts 60-70°C above the solidus contain about 16% TiO₂ at 20-25 kb. The melt mass must be increased by about 15% by melting olivine ± orthopyroxene beyond the ilmenite-out curve in order to reduce the TiO₂ content of this melt to 13.5% TiO₂ and to undersaturate the melt with respect to ilmenite. The total amount of melting is determined by the modal content of ilmenite. If, for example, the mode of ilmenite is 2 wt% (= 1.1 % TiO₂) then about 6% melting is required to reach the ilmenite-out curve and an additional 1% to attain the Red glass composition. Doubling the ilmenite mode doubles the amount of melting.

Using the same arguments, the melt mass must be increased another 2.5 times beyond that at the ilmenite-out curve to reproduce the observed TiO₂ (4.6) contents of the Apollo 14 Yellow glass. If the mode of ilmenite in the source was 1%, the total amount of melting was about 14%, 71% of which from melting TiO₂-poor phase(s). If the TiO₂-poor phase melted was olivine, then the CaO and Al₂O₃ contents of the ilmenite-saturated melts would be 26% and 20% respectively. Melts with such high CaO contents are not obtained from lherzolite. If the TiO₂-poor phases are olivine and diopside, then CaO contents of ilmenite saturated melts are buffered at much lower values. But no known mare picrite glass has diopside within 100° of the liquidus. The most reasonable model is that the CaO and Al₂O₃ contents are buffered by an olivine and orthopyroxene residuum, as permitted by the phase equilibria. It is concluded that the mare glasses were equilibrated with orthopyroxene and probably olivine and that the mean depths of segregation are 400-500 km.

Table 1

P(Kb)	(1)	(2)	(3)
10	22%	30%	38%
20	20	25	29
25	19	-	

TiO₂ (wt%) contents of ilmenite saturated liquidus for Apollo (1) 15 Red (13.5% TiO₂); (2) 17 Orange (9% TiO₂); (3) 14 Yellow Glasses (4.6% TiO₂)

Table 2

P(kb)/T(°C)	10/1180	20/1280	30/1380
	10%	12%	12%

TiO₂ contents (wt%) of the mare basalts along the ilmenite "lherzolite" solidus

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